

Laboratory Name: Argonne National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP:

Electron Microscopy Center for Materials Research

FWP Number: 58405

Program Scope: Conducts materials research using advanced microstructural characterization methods based on electron beams. The emphasis of this research is on the role of microstructure and defect structure on materials behavior. In addition, the EMC maintains unique resources and facilities for scientific research, and develops new capabilities in instrumentation, techniques, and scientific expertise.

Major Program Achievements (over duration of support):

Aberration correction in electron microscopy has been advanced by studies of lens design and sample/space configurations aimed at significantly advancing *in situ* experimentation as part of the Transmission Electron Aberration-corrected Microscope (TEAM) project. A new lens design has been proposed that offers new capabilities for *in situ* science, and further evaluation of this design is underway.

New methods for quantitative electron imaging and diffraction have been developed. New studies have shown the significant contribution of inelastically scattered electrons to defect images, and elastic diffusely scattered electrons to diffraction from individual nanoscale defects. Lorentz STEM has been developed as a method to image domains of electric or magnetic fields has been developed and tested on nanoscale magnetic structures. Scanning Confocal electron microscopy has been developed to image structures to a resolution of <100 nm in samples of considerable thickness (eg. 8 μm). Advantages over x-ray microscopy include convenience and speed of data collection.

Significant improvements in understanding defect processes have been achieved through *in situ* studies. Defects formed under elevated temperature ion and neutron irradiations have been found to explain radiation hardening by dislocation pinning. Formation of nanoparticles by single ion impacts has been discovered to occur and is best understood by a shock wave formed by near surface cascade events. Grain boundary migration has been revealed to include collective motion of up to several hundred atoms by *in situ* high-temperature high-resolution TEM.

Program impact:

Developments in analytical spectroscopy, quantitative TEM, and *in situ* experiments are well recognized, as are defect studies by TEM methods. Many capabilities of the current generation of intermediate-voltage analytical microscopes are attributed to advances made in this program.

TEM studies of oxide superconductors have been particularly important in understanding pinning defects, grain boundaries, and Josephson junctions, yielding insights into both fundamental mechanisms and applications.

Interactions:

As a national user facility, the EMC typically interacts with more than 100 users per year.

Strong research collaborations include: Oak Ridge, Ames, LANL, Sandia; UIUC, NWU, UND, UCin, Upitt, Bechtel Bettis; UOx (UK), ANSTO (Australia), INP (Uzbekistan), USalford (UK).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):

Invited book published: Characterization of Radiation Damage by Transmission Electron Microscopy, M L Jenkins and M. A. Kirk, Inst. of Physics Publishing, Bristol, 2001.

C. Allen, elected Fellow, ASM-International, 2000.

Personnel Commitments for FY2002 to Nearest +/- 10%:

C. W. Allen (100%), B. Kabius (100%), M.A. Kirk (50%), D.J. Miller (65%), N.J. Zaluzec (75%); R. E. Cook (100%), R. Csencsits (50%), L. Funk (50%), J. Hiller (100%), and A. McCormick (100%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$1,878,000

FY01 BA \$2,203,000

FY02 BA \$2,160,000

Laboratory Name: Argonne National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP:

Atomic Structure in Glasses through Fluctuation Microscopy

FWP Number: 58406

Program Scope: Development and application of Fluctuation Electron Microscopy (FEM) to address important problems in glasses and amorphous materials, in particular, the role medium range order plays on the properties and crystallization of amorphous materials. The program has concentrated on the structure of amorphous silicon and the role MRO plays in these materials, and has also included studies on the structure of amorphous metallic glasses and the modification of amorphous structure and the corresponding effects on properties and crystallization behavior.

Major Program Achievements (over duration of support):

Developed the capability for directional scans in reciprocal space, furthering ability to study short-range order. This first demonstration of directional scan fluctuation microscopy was applied to Ni/Mo samples.

Demonstrated that amorphous Si prepared by ion implantation is not truly a random structure, but instead has extensive medium-range order (MRO). The formation of this topological order has a strong dependence on ion mass, according to the experimental evidence that the degree of MRO is larger for heavy ion damage than for light ion damage. This finding is consistent with the theoretical work by molecular dynamic simulations and can be explained by an energy spike model.

Identified differences in the structure of aluminum oxide formed in oxygen and that formed in ozone. Demonstrated that the oxide grown with ozone has a higher density and a higher degree of medium-range order. These results suggest the basis for better passivation behavior in ozone-produced aluminum oxide. This result disagrees with common belief that more homogenous oxides will provide better passivation behavior.

Program Impact:

Provided insights into the medium range order of amorphous materials. This information, which cannot be obtained by any other method, has led to an improved understanding of macroscopic properties of amorphous materials based on microscopic structure. This technique is now being pursued by several other groups..

Interactions:

Sandia National Laboratory (J. Sullivan, T. Friedmann)
Ames National Laboratory (C. Jenks, M. Kramer, D. Sordélet).
University of Pittsburgh (J. Yang)
University of Cincinnati (V. Vasudevan)
University of Illinois-Champaign-Urbana (J. Birrell, J. Chang).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Invited talk, 2002 APS March Meeting (Dr. J. Sullivan, Sandia)

Personnel Commitments for FY2002 to Nearest +/- 10%:

D.J. Miller (20%), X. Chen (Post-doc during first third of FY, then visiting scientist, 100%), J. Chen (graduate student, 50%), J. Birrell (graduate student, 50%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$0

FY01 BA \$200,000

FY02 BA \$196,000

Laboratory Name: Argonne National Laboratory
B&R Code: KC020101

FWP and possible subtask under FWP:

Nonequilibrium Materials: Formation and Properties, Defect-Property Correlations

FWP Number: 58445

Program Scope:

Fundamental understanding of particle-solid interactions and defects is used to develop and expand our ability to fabricate nonequilibrium and nanoscale materials and control their behavior. Patterning with particle beams is used to fabricate structures in important systems ranging from metallic alloys to complex oxides. Quantitative knowledge of the production, structure and kinetics of point defects, defect aggregates, and precipitates, and their subsequent effects on mass transport is required for tailoring a wide variety of complex materials systems. Characterization of defect interactions and dopants introduced by ion beam processing will be of importance to many applications such as control of embedded nanoparticle formation and patterning.

Major Program Achievements (over duration of support):

Single ion impacts have been observed with the intermediate-voltage electron microscope-tandem. Nanoparticle ejection by single ion impacts has been quantitatively measured and correlated with crater formation. The size distribution of ejected nanoparticles has an inverse power-law with an exponent of -2 independent of total sputtering yield. This indicates that the clusters are produced when shock waves, generated by sub-surface displacement cascades, impact and ablate the surface. The implication is that the nanoparticles are unaltered bits of the surface.

High resolution TEM studies of rare gas nanoparticles embedded in Al dramatically demonstrated that atomic displacements change precipitate morphology and structure as a direct result of changes in Al cavity surface area. Coalescence of solid precipitates results in total volume, not surface area, being conserved, implying that surface tension is not dominant energetically. Liquid Xe nanoprecipitates exhibit two-dimensional atomic ordering at the Al interface that appears to be due to geometric constraint and not interaction with the Al atoms on the cavity surface.

Nanocluster formation during heavy ion bombardment of a thin contiguous Ag layer sandwiched between two continuous SiO₂ layers has been observed using the in-situ IVEM-Tandem. Plastic flow of the Ag film enlarges pre-existing pinholes and separates the film at grain boundaries transforming the as-deposited thin Ag film into three-dimensional microcrystals having diameters greater than 30 nm. In addition, ballistic recoils continually inject Ag atoms into the SiO₂ where they precipitate into nanoclusters.

Columnar defect morphology in YBCO after annealing at 600°C results in a J_c increase as much as 5 times were demonstrated at the intermediate annealing temperature of 450°C. TEM shows evidence of a high density of nano-twins connecting adjacent columnar defects.

Program Impact:

Provided insights on ion solid interactions and nanostructure stability and properties.

Interactions:

C. W. Allen (58405), S. E. Donnelly (U. Salford, UK) K. Furuya (NIMS Japan), L. Thomé (Orsay, France), L. Paulius and A. Petrean (Western Michigan U.), M. G. Burke (Bettis), M. Jenkins (U. of Oxford), E. Ibragimova (Institute of Nuclear Physics, Tashkent), L. Paulius (Western Michigan U.), K. Goretti (ANL), B. Riley (American Superconductor), D. Caplin (Imperial College, London)

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

More than 10 invited talks since 2001

Personnel Commitments for FY2002 to Nearest +/- 10%:

R. C. Birtcher (100%), L. E. Rehn (100%), P. Baldo (100%), L. Funk (50%), B. J. Kestel (50%), M. A. Kirk (50%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$1,598,000.

FY01 BA \$842

FY02 BA \$825

FWP and possible subtask under FWP:

Interfacial Materials

FWP Number: 58307

Program Scope: This program combines advanced materials synthesis, characterization and properties measurement techniques with computer simulations to elucidate how materials microstructure and the underlying interfacial structure and composition control the physical properties of ceramic thin films. The ability to manipulate the film microstructure, from single crystalline to random or columnar coarse-grained or nanocrystalline, represents a unique feature of the program. The complementary strengths of simulation and experiment are exploited to provide atomic-level insights into the concepts, mechanisms and interfacial driving forces that control the overall film properties (e.g., thermo-elastic behavior, electrical behavior, corrosion and wear resistance)..

Major Program Achievements (over duration of support):

In-situ growth studies of complex oxides: Using a unique in situ processing facility developed at the Advanced Photon Source, major advances have been made in the understanding of oxide and nitride thin film growth processes and in controlling phase transformation behavior and domain structure development in ferroelectric thin films.

Atomistic simulation of ferroelectric perovskites: The first molecular-dynamics simulation method for studying ferroelectricity in perovskite materials has been developed and used to study solids solutions and heterostructures.

Multiscale simulation of polycrystalline materials: A novel multiscale computational approach that incorporates all the relevant length and time scales has been developed, enabling the prediction of microstructural evolution in polycrystalline materials under the driving forces of stress and temperature. This effort is closely connected with the BES Computational Materials Science Network (CMSN).

Atomic-level structure and properties of grain boundaries: High-resolution electron microscopy has been used to study the structure of grain boundaries (GBs) in ceramics and metals and the mechanisms of GB migration.

Thermal transport in solids and liquids: Significant improvements in the control of thermal transport in solids and fluids have been obtained through both experimental and simulation investigations of nanostructured materials. We found that thermal transport can be enhanced in liquids containing small quantities of dispersed nanoparticles.

Program Impact:

By combining advanced experimental tools and simulation, we have developed an unprecedented understanding of the impact of specific defects (grain boundaries, nonstoichiometry, interfaces) on materials behavior. We have established metal-organic chemical vapor deposition as a premier method for the fabrication of extremely high-quality complex oxide films; our samples being recognized as standards against which all other films are judged.

Interactions:

Northern Illinois U., Purdue, Northwestern., U. Wisconsin, North Carolina State U., UCSB, U. Colorado, U. Illinois-Chicago, U. Houston, U. Maryland, U. North Carolina-Chapel Hill, U. Wisconsin-Milwaukee, Rensselaer Polytechnic Institute, MIT, Penn State., U. Pittsburgh, LBL, INTEL, TI, Structured Materials Industries, U. Rosario (Argentina), Imperial College (London), Forschungszentrum Karlsruhe (Germany) and MPI Stuttgart (Germany).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

DOE Basic Energy Sciences Award for Sustained Outstanding Research in Metallurgy and Ceramics (Wolf); Fellowships of American Physical Society (Wolf, Merkle) Max-Planck Research Award (Wolf); 50k\$ award from DOE for "chunky bullet" (Wolf and Phillpot); 1 US patent (Eastman); more than 70 invited talks in 2000-2002.

Personnel Commitments for FY2002 to Nearest +/-10%:

O. Auciello (50%), G. Bai (Scientific Associate, 50%), J. Eastman (100%), K. Merkle (90%), S. R. Phillpot (100%), S. Streiffer (30%), L. Thompson (100%), D. Wolf (Group Leader, 60%), V. Yamakov (Postdoc 70%), H.-S. Yang (Postdoc, 70%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$1,644,000

FY01 BA \$1,595,000

FY02 BA \$1,729,000

FWP and possible subtask under FWP:
Proximity Interactions at Oxide Boundaries

FWP Number: 58930

Program Scope: Proximity interactions across boundaries, including strain fields and interface driven electronic structure changes, are studied in bicrystal grain boundaries, thermally grown oxides, thin film multilayers and nano-objects. The evolution and adhesion of thermally-grown protective oxides are studied, with emphasis on effects of cross-current diffusion, dopants, growth stresses and the oxygen activity gradient. Oxide multilayers and nanodots are fabricated and investigated. Grain boundary properties of bulk ceramics are studied; joining techniques are developed. Future effort will focus on the development of a predictive understanding of the physical and chemical processes that control alloy oxidation from early stages of oxidation to the mature, "steady state". A unique combination of *in situ* x-ray and ion scattering tools, electron microscopy, and multiscale-simulation will be used to study key interfacial processes and phenomena.

Major Program Achievements (over duration of support):

Elucidated influence of a "reactive element" dopant on cross current diffusion behavior in thermally grown aluminum and chromium protective oxides. For example, reactive elements, diffused into grain boundaries, were found to alter relative oxygen/metal diffusion rates, modifying oxide growth characteristics. Pioneered new x-ray techniques, including grazing exit x-ray fluorescence and *in situ* x-ray diffraction, for investigating fundamentals of alloy oxidation. Isolated grain boundaries of YBa₂Cu₃O₇ were modified with oxygen and/or cation doping to study strain and hole doping effects. YBa₂Cu₃O₇ monoliths were successfully joined with near atomic-scale registry across the joint. The complicated magnetic field dependence of critical currents in high-T_c superconducting grain boundaries was explained in terms of a pinning interaction with Abrikosov vortices near the grain boundary (a mechanism first proposed by A. Gurevich). Strain was demonstrated to influence magnetization and lead to enhanced magnetoresistance across grain boundaries in manganites.

Program Impact:

This program is providing key insight into oxidation processes not achievable in earlier *ex situ* studies. Insights achieved from the oxidation and grain boundary studies may be important for the development of improved high temperature protective oxide coatings, for HTS wire development (a focus effort in EERE-Electric Systems), and for magnetic memory technology.

Interactions:

University of Pittsburgh, University of Illinois-Urbana Champaign, University of California-Santa Barbara, Oklahoma State University, Lawrence Berkeley Laboratory, Oak Ridge National Laboratory, Sandia National Laboratory, Idaho National Engineering and Environmental Laboratory, University of Wisconsin.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

B. W. Veal and A. P. Paulikas: Listed in Science Watch (vol. 8, p. 1, 1997) among 30 most cited scientists in the physical sciences (1990-1996). B. W. Veal: ANL Exceptional Performance Program, 1992 and 1996. Conference co-organizer and editor. Recent Invited talks: Am. Phys. Soc., Minneapolis, Mar. 20-24, 2000; 104th Mtg. of the Am. Ceram. Soc., St. Louis, April 28-May 1, 2002. K. Gray and B. W. Veal: Fellow of the American Physical Society. K. E. Gray: Honorary Visiting Professor, Chinese Academy of Sciences, Beijing, Oct. 2002; 7 invited talks in last 3 years. D. J. Miller: 17 invited talks since 1997.

Personnel Commitments for FY2002 to Nearest +/- 10%: P. Berghuis (75%), K.E. Gray (20%), D.J. Miller (20%), B.W. Veal (100%), A.P. Paulikas (100%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$869k

FY01 BA \$745k

FY02 BA \$668k

Laboratory Name: Argonne National Laboratory
B&R Code: KC020201

FWP and possible subtask under FWP: Neutron and X-ray Scattering

FWP Number: 58701

Program Scope:

Members of the neutron and x-ray scattering group enable the Division to pursue strong multidisciplinary research programs that require scattering techniques to be combined with creative synthesis of new materials, theory, and other experimental tools. Priority is given to research that anticipates the capabilities of the SNS. World-wide neutron and x-ray scattering facilities are used. Group members also operate three research instruments at the IPNS, serving a broad user community. An important goal of the group is to strengthen the neutron-user community in the US. Group members also participate in specification, design, and review of instrumentation for the SNS.

Major Program Achievements (over duration of support):

Superconductors. Lattice properties as a function of temperature and pressure and phonon density of states have been determined for the newly discovered 39K superconductor MgB_2 . This work, combined with work done in other groups in MSD, leads to an understanding of how such a high T_c can be achieved through electron-phonon coupling in this material.

Colossal Magnetoresistive Materials. Neutron and x-ray scattering has been used to investigate the complex interactions between charge, orbital, magnetic, and strain degrees of freedom in both layered and perovskite manganites that display colossal magnetoresistance. Diffuse scattering techniques have revealed nanoscale self-organization of polarons into extended defect structures that "melt" in magnetic field.

Strongly-Correlated Electron Systems. Neutron and muon measurements of some cerium heavy fermion compounds have shown that extreme anisotropy can profoundly affect the spin dynamics in ways that are predicted by the Anisotropic Kondo Model. The experiments provide novel insight into the nature of "hidden order", which is a major unsolved problem in strongly correlated electron physics.

Magnetism in Thin Films and Multilayers. Neutron reflectometry has been used to explain the magnetic phase diagram of exchange coupled superlattices and the hysteresis cycle of exchange biased, ferromagnetic thin films. Specifically, the evolution of the magnetization after the surface spin flop transition in a finite antiferromagnetic superlattice was determined, providing a basis for further theoretical work in this field.

Polymeric and organic membranes. A new technique, combining reflectometry with spin-echo, is being developed to study the structure of polymeric and organic membranes. Following a "proof of principle" experiment, a spectrometer is being readied at the Institut Laue Langevin -in collaboration with the Max Planck Institut of Stuttgart- to prove the scientific case and move toward an SNS instrument design.

Program Impact:

Work of the group in many different science areas is recognized world wide as leading the field and opening new research directions. Close interaction with new-materials synthesis, other experimental work, and theory is a widely-recognized strength of the group. The impact of research done by the group is evidenced by over 120 archival publications and 48 invited talks at major meetings during 1999-2002.

Interactions:

Group members collaborate with most other groups in the Division and with a large number of scientists at universities and other national laboratories, as evidenced by over 230 coauthors on papers published 1999-2002.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

J. Jorgensen: Among 100 most highly cited physicists (ISIhighlycited.com). G. P. Felcher: Humbolt Award, 1999.

Personnel Commitments for FY2002 to Nearest +/-10%:

J. D. Jorgensen (Group Leader) (100%), G. P. Felcher (100%), R. Osborn (80%), S. Rosenkranz (100%), S. Short (100%), S. G. E. te Velhuis (100%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$1156K

FY01 BA \$1915K

FY02 BA \$1863K

FWP and possible subtask under FWP:

Synchrotron Radiation Studies

FWP Number: 58926

Program Scope: This program develops new capabilities using the nation's synchrotron radiation facilities and applies them to cutting-edge problems in materials science. In particular, we aim to play a leading scientific role at the Advanced Photon Source (APS). X-ray scattering studies take advantage of the high brilliance APS x-ray source for *in-situ* and time-resolved studies of surface and thin film structure. High-resolution angle-resolved photoemission is used to understand the nature of superconductivity in the hi- T_c materials. New thrusts focus on exploring science enabled by future facilities such as an x-ray nanoprobe, a high-energy photoemission microscope, and a coherent, femtosecond x-ray source.

Major Program Achievements (over duration of support):

Vapor-Phase Epitaxy. We have used *in situ* x-ray scattering to understand the atomic-scale growth mechanisms and surface structures occurring during MOCVD growth of GaN and PbTiO₃. Homoepitaxial growth mode transitions and surface reconstructions were mapped as a function of process conditions for the first time.

Electrocatalytic Surfaces. *In situ* x-ray scattering during electrodeposition and electrocatalysis was used to understand the structures and catalytic mechanisms in systems such as Rh/Au and RuO₂ under electrolytes. We observed surface structures responsible for hydrogen and oxygen evolution, surface redox processes, and an unexpected reversible activation of RuO₂ (110) surfaces that involves conversion of Ru between +3 and +4 valance states.

Quasiparticles in High- T_c Superconductors. The nature of the carriers in high- T_c superconductors has been elucidated using angle-resolved photoemission. We have identified a particular point on the Fermi surface where the superconducting energy gap vanishes below T_c , and determined the nature of the excitations that dominate the properties of the system.

New Methods in Angle-Resolved Photoemission. The unconventional nature of the electronic structure of the cuprate superconductors, coupled with the small size of their Brillouin zones, makes accurate determination of the Fermi surface by angle-resolved photoemission rather difficult. We have developed several new methods for the determination of the Fermi surface, making possible detailed measurements of new complex materials.

Time-Correlation Spectroscopy with Coherent X-rays. We have developed this new technique for observing atomic- and nano-scale dynamics and used it observe non-linear diffusion in concentrated colloids and fluctuations during domain coarsening. These studies with coherent x-rays are providing part of the scientific basis for the next generation of synchrotron x-ray sources.

Program Impact:

The Synchrotron Radiation Studies group publishes an average of 30 refereed articles every year, typically including 4 articles per year in Physical Review Letters or Nature. These articles are highly cited; based on citation rate, our average paper is in the top 1% of papers in materials science.

Interactions:

This project provides expertise in synchrotron techniques to collaborations with several Materials Science Div. groups (esp. FWP 59001, 58305, and 58936), other ANL Divisions (esp. Experimental Facilities), and with researchers at more than 30 universities, academic institutions, and industrial laboratories worldwide. In the past three years more than 20 students and postdocs have performed research as members of our group.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

J. C. Campuzano was appointed Scientific Director of Univ. of Wisconsin's Synchrotron Radiation Center in 2002. Each year about two dozen invited talks are given by group members.

Personnel Commitments for FY2002 to Nearest +/-10%:

Staff: J. C. Campuzano (50%), P. H. Fuoss (60%), Z. Nagy (40%), H. You (90%), G.B. Stephenson (50%);

Visiting Faculty: M. Bedzyk (10%), W. Lowe (30%); Postdoc: D. Fong (40%); Secretary: J. Cowan (50%).

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$914,000

FY01 BA \$962,000

FY02 BA \$993,000

FWP and possible subtask under FWP:
Ceramic Epitaxial Films

FWP Number: 58305

Program Scope: Experiments combined with computer simulations are used to elucidate the processing-structure-properties relationships of complex-oxide thin films and layered heterostructures prepared by MOCVD, sputter deposition and chemical solution deposition. Our main emphasis is on ferroelectric, high-dielectric-constant and low-loss perovskite oxides. The goal is to use thin-film microstructure in well-defined model systems to manipulate film dielectric, ferroelectric, pyroelectric, electro-optic and acousto-optic behavior as a function of crystallographic orientation and film microstructure, from epitaxial single-crystalline to columnar or random poly- or nanocrystalline. Results from these studies, combined with comparison of film response to that of bulk single crystals, enables us to gain fundamental understanding of the effects of interfaces on the physics of complex oxides. This includes insight into the mechanisms of strain accommodation, e.g., through dislocation and twin formation. These investigations provide the basis for optimization of materials properties relevant to device applications. Another key element of this program is the utilization of sophisticated x-ray scattering techniques at the Advanced Photon Source. This FWP is closely coordinated with FWP 58307 (Interfaces in Advanced Ceramics).

Major Program Achievements:

In-Situ Characterization of Complex-Oxide MOCVD. In collaboration with MSD's Synchrotron Radiation Studies Group and in close coordination with FWP 58307, a facility for in-situ x-ray studies of MOCVD thin-film growth, post-growth thin-film processing and environmental effects has been developed at the APS-BESSRC beam line 12ID-D. Major highlights to-date include: 1) Exploration of MOCVD growth modes and film microstructure as a function of MOCVD process parameters. 2) The crystallography of the stable Pb-terminated surface of PbTiO_3 has been measured, and a reconstruction based on stabilization of an antiferrodistortive R_{25} mode in the top unit cell has been identified. 3) In FY02, we have upgraded this system with an additional precursor delivery source. We have begun synthesis of ferroelectric/antiferroelectric superlattices consisting of PbTiO_3 / $\text{Pb}(\text{Ti,Zr})\text{O}_3$ heterostructures.

Studies of Ferroelectric Domain Switching Using Synchrotron X-Ray Scattering. In experiments carried out on the BESSRC-CAT undulator beamline 12-ID-D, we have performed very fast (1ns) time-resolved studies of the structural deformations induced by polarization reversal in ferroelectric thin films under an applied electric field, by utilizing a very high speed rotating crystal beam chopper developed by SRI-CAT. In FY02, we combined this technique with x-ray focusing using Kirkpatrick-Baez mirrors, to achieve approximately 5 micron spatial resolution. Approximately one order of magnitude better spatial resolution can be achieved with optimization of the focusing optics on our setup, using demonstrated technologies.

Program Impact:

Our work on ferroelectric thin films is recognized world-wide not only for the fundamental insights it is providing on the controlled synthesis and the nature of ferroelectricity in thin films, but also on its impact on forefront technological applications.

Approx. 60 publications, 5 books/proceedings, 3 invited review chapters in the past three years.

Organized 10 international symposia, including the 13th International Symposium on Integrated Ferroelectrics (2001) the Fall 2001 MRS Ferroelectric Thin Films Symposium, and the Pan-American Advanced Studies Institute on Science and Technology of Ferroelectric Materials, held in Rosario, Argentina, Sept. 2002.

Interactions:

This program has strong interactions and collaborations with MSD programs on Molecular Control of Synthesis (57504), Synchrotron Radiation Science (58926), and with ANL's Energy Technology Division. It also has strong collaborations with university programs at Northern Illinois Univ., Northwestern, U. Wisconsin-Madison, North Carolina State Univ., Penn State Univ., University of North Carolina-Chapel Hill, U. Maryland, University of California-Santa Barbara, and Rice University; and with industry (Ionwerks, Symetrix, Ramtron, Texas Instruments, Agilent, Motorola). Lead laboratory and Co-Coordinator (with Sandia) for CSP Project "Nanoscale Phenomena in Perovskite Thin Films".

Recognition, Honors, and Awards (at least partly attributable to support under this FWP or subtask):

Integrated Ferroelectrics 2000 Award presented to O. Auciello; 40 invited talks over the past three years.

Personnel Commitments for FY02:

O. Auciello (30%), G. Bai (Scientific Associate, 35%) S. Streiffer (40%)

Authorized Budget (BA) for FY00, FY01, and FY02:

FY00: \$227 K

FY01: \$388 K

FY02: \$197 K

FWP and possible subtask under FWP:

Naturally Layered Manganites

FWP Number: 58802

Program Scope:

The Naturally Layered Manganite Program explores the connections among spin, charge, and lattice in layered colossal magnetoresistive (CMR) oxides. Our collaborative research team has made rapid exploration of these oxides and are expanding into related systems with emphasis on both bulk and surface/interface properties.

Synthesis and crystal growth under control of stoichiometry and crystal quality provides high-quality materials for sophisticated measurements of physical properties. Future directions will involve studies of new oxide materials, including cobalt oxides that exhibit spin-state transitions as well as charge, spin, and orbital order.

Scattering experiments utilize both neutrons and x-rays to study microscopic interactions with an emphasis on short-range charge-, spin-, and orbital-ordering. Such studies generate input for new materials design, theoretical models, and complementary magnetic and transport studies.

Detailed transport and magnetization studies directly target the mechanisms of CMR, the nature of the metallic state, and how magnetic order on long- and short-range connect to these bulk properties.

We are initiating a scanning tunneling microscopy effort to investigate surface electronic states and have begun a characterization of the metallic and insulating manganite phases. These studies will usher in future thin-film and nanostructures in which 100% spin-polarized carrier injection will be a critical objective.

Major Program Achievements (over duration of support):

Determination of Structural and Magnetic Phase Diagram We successfully extended the solubility range of layered manganites into the highly Mn^{4+} regime, mapping the structural and magnetic phases. This phase diagram identifies key materials for crystal growth and exploring ordering phenomena on varying length scales.

Nature of Conductivity Transport studies in selected single crystal compositions of layered manganites enabled seminal results, including validation of the double-exchange selection rule, development of a simple spin-wave model including double exchange, and demonstration of the metallic nature of conduction below T_C .

Charge Correlations, Polarons, and CMR Using the complementarity of x-ray and neutron scattering, we have determined the structure of atomic displacements caused by nanoscale polaron correlations in the paramagnetic phase of bilayer manganites and have established that the orbital polarization switches from perpendicular to the conducting planes to parallel as the magnetic transition is approached on cooling.

Program Impact:

As world leaders in the field, our collaborative program has helped to define the direction of CMR research. Both directly and through external collaborations this program has produced high-impact results as measured by:

Over 60 refereed papers, over 40 invited talks, and two invited book chapters since program inception in FY97.

Two invited review articles recognized by cover status (*MRS Bulletin*, Dec. 1999, *J. Phys. Chem. B*, Nov. 2001)

Widespread recognition reflected in over 930 total citations. Six papers exceed 50 citations; one claims 138.

The program adds value to allied projects in MSD, including Neutron and X-ray Scattering (58701), Emerging Materials (58916), and Magnetic Thin Films (58918). We collaborate closely with the APS and IPNS Divisions and the EMC. Our program impacts research programs at universities worldwide (>40 external collaborators).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

John F. Mitchell received one of the prestigious Presidential (and DOE) Early Career Awards in 2000.

Kenneth E. Gray and John F. Mitchell were elected as Fellows of the American Physical Society in 2000 and 2002.

Personnel Commitments for FY2002 to Nearest +/- 10%:

J.F. Mitchell (50%), R. Osborn (20%), K. Gray (10%), S. Bader (10%), H. Zheng (50%), D.N. Argyriou(10%), J. Burley (100%), J. Gu (50%), E. Badica (100%), B. Campbell (80%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$682K

FY01 BA \$756K

FY02 BA \$692K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020202

FWP and possible subtask under FWP:

Physics of Granular Materials

FWP Number: 58806

Program Scope: The Physics of Granular Materials program examines the fundamental properties of granular media. More detail is available at www.msd.anl.gov/groups/sm/granphy. We focus on the following topics:

Dynamics of thin layers of granular materials. We explore traditional mechanical vibration technique and novel ac gas-fluidization method. This project includes theoretical modeling and experimental studies.

Self-assembly and patterns in electrostatically driven granular systems. This project focuses on theoretical and experimental studies of conducting and dielectric grains in strong electric fields in vacuum or submersed in poorly-conducting liquids.

Theoretical description of avalanches and slow granular flows based on novel Ginzburg-Landau type approaches for onset of fluidization. The model parameters are derived from large-scale molecular dynamics simulations performed at BES National Energy Research Supercomputing Center.

Theoretical and experimental studies of phase separation in granular systems.

Major Program Achievements (over duration of support):

We pioneered a novel approach to the description of granular materials. For the first time we succeeded in describing localized excitations (oscillons, interfaces) and periodic structures (squares, stripes, hexagons) in vibrating thin granular layers within the same framework. Based on our model we predicted that the interface between out-of-phase vibrating flat layers would move under the application of small sub-harmonic signals. We later confirmed this prediction experimentally.

We initiated the first experimental studies of dynamics of granular materials in strong electric fields. We discovered new phase transitions between the granular gas and solid, as well as the formation and coarsening of clusters. Later we performed molecular-dynamics simulations and developed a theoretical description of these phenomena. Now we extend our studies towards self-assembly of microparticles in poorly conducting liquids.

We developed a novel approach to shear granular flows and avalanches. Based on a combination of momentum conservation laws and the order parameter equation for the degree of fluidization, our framework correctly captured the shape of avalanches, transitions from triangular to up-hill avalanches, flow velocity distributions and other features. The prediction for a finite minimal value of the up-hill avalanche front velocity was confirmed experimentally. We developed large-scale MD simulations to validate the theoretical model.

Program Impact:

Our work on granular materials is recognized worldwide. Initiated about three years ago, our phenomenological approach to non-equilibrium phenomena in general, and granular materials in particular, became a legitimate theoretical tool in the scientific community. Our mode of operation combining strong theory and precise experiment within one group has become a hallmark of our research.

Interactions:

University of California at San Diego; University of Kansas; Los Alamos National Laboratory ; Clark University, Massachusetts; Hebrew University of Jerusalem, Israel ; CEA Saclay, France

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

More than 15 papers in Phys. Rev. and Phys. Rev. Lett., about 110 citations, 16 invited talks

Organized five workshops on dynamics of granular materials

DOE granted our proposal (with LANL, SNL and Ames Lab) for a Center of Excellence on Granular Flows and Kinetics in FY01.

50,000 hours CPU time grant from National Energy Research Supercomputing Center

APS Fellowship to I. Aronson

Personnel Commitments for FY2002 to Nearest +/-10%:

Aronson 90%, W. K. Kwok 15%, V. Vinokur 10%, M.V. Sapozhnikov 100%, J. Lie 100%, D. Rosenmann 25%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$

FY01 BA \$605K

FY02 BA \$624K

FWP and possible subtask under FWP:

Mesoscopic Superconductivity

FWP Number: 58823

Program Scope:

The mesoscopic superconductivity program explores the qualitatively new behavior that occurs in superconductors at small length scales where effects from confinement, proximity, and collective behavior dramatically alter the physical properties and response of the material. Currently, we are focusing on (i) confinement effects of vortex matter in structures with dimensions comparable to the penetration depth and the Abrikosov length scale, (ii) proximity effect at interfaces of hybrid structures of magnetic and superconducting materials and (iii) collective behavior in arrays of mesoscopic superconducting dots where new phenomena are anticipated to arise from the interaction of meso-patterned materials. In addition, we develop new instrumentation based on micro-electromechanical systems (MEMS) technology.

Major Program Achievements (over duration of support):

Confinement: A novel STM geometry with a superconducting tip and a normal substrate has uncovered an unexpected periodic change in the zero bias density of states (DOS) of the superconducting gap in a magnetic field. The periodicity is tied to the penetration of the normal vortex cores into the superconducting tip. Based on this discovery, we designed a new non-dissipative quantum current switch for superconducting quantum wires operating in the ballistic regime

We have succeeded in directly imaging a single vortex being pinned by a columnar defect induced by heavy ion irradiation in NbSe₂ using a low temperature STM. Our results can be used to investigate vortex core pinning in superconductors.

Collective behavior: We have examined superconducting Nb-films on Anodic Aluminum Oxide (AAO) -substrates with S. Jiang (FWP58918) and J. Xu (Rutgers University). Step-wise variations in the critical current have been observed in magnetization and magneto-transport measurements at matching fields up to 1 T, the highest matching field reported thus far.

Nano-wires: Pb nano-wires with diameters ranging from 50 to 200 nm were fabricated using electrodeposition into AAO templates. These wires display a substantial enhancement of the critical field, and step-wise superconducting transitions that can be associated with flux quantization in confined geometries.

Avalanches: The penetration of magnetic flux into superconducting films has been investigated using a high-resolution magneto-optical imaging technique. At low temperatures, break-down in the form of thermo-magnetic avalanches is observed. The front of these avalanches displays fractal behavior characterized by a fractal dimension of 2.4 and roughness exponent of 1.4. The introduction of periodic arrays of holes dramatically structures the microscopic flow directions of the avalanche. This opens new approaches to studying non-linear avalanche dynamics. (I. Aronson, FWP 58806 V. Vinokur, FWP 59002 MTI).

MEMS: We fabricated of a prototype micro-positioning device using thermally driven 'actuators' that produce motion by the differential thermal expansion of two legs of a polysilicon ladder that are heated to different temperatures. Using a combination of multiple actuators working in synchronization, we designed an x-y micro-positioning platform for the STM.

Program Impact:

Invited talks: on the MEMS results at the March 2001 meeting of the APS in Seattle, WA; on the STM results at the Frontiers in Research 2000 meeting in Irvine, CA; on the avalanches at the International Workshop on Vortex matter in Inhomogeneous Superconductors, Bordeaux, France, Dec. 2000; on the Nb/AAO results at LT23 in Hiroshima, Sept 2002.

Interactions:

This is a multi-disciplinary research program involving numerous collaborations within the Materials Science Division (58906, 58918, 58806, 59002 and the Electron Microscopy Center), and with external collaborators at the Univ. of New Mexico-Albuquerque, Univ. of Minnesota, Univ. of Notre Dame, Univ. of Chicago, Texas A&M Univ., Rutgers University.

Personnel Commitments for FY2002 to Nearest +/- 10%:

W. K. Kwok 25%, G. Karapetrov 85%, M. Iavarone 70%, U. Welp 30%, A. Koshelev 15%, V. Vlasko-Vlasov 25%, D. Rosenmann 25%; Z. Xiao 65%.

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$

FY01 BA \$353K

FY02 BA \$293K

FWP and possible subtask under FWP:

Laterally Confined Nanomagnets

FWP Number: 58830

Program Scope: The program explores and develops new approaches to the fabrication, characterization, and understanding of magnetic materials on the nanoscale, encompassing lithographic patterning and self-assembly. Basic issues are addressed at the frontiers of the emerging field of *laterally confined nanomagnets*. The task is to identify the fundamentally new physical phenomena associated with the competition between spatial and magnetic length scales and proximity effects. The goal is to understand the ultimate limits of miniaturization, including the interactions between elements in a nano-array, as well as the internal structure of individual, isolated units, and to work to transform the art of nanomagnet fabrication into a science. The new physical phenomena explored should substantially extend our basic understanding of nanostructured magnetic materials and lay the foundations for new technologies.

Major Program Achievements (over duration of support):

Tailoring exchange bias via shape anisotropy: The exchange bias of Fe stripe arrays on antiferromagnetic FeF_2 was investigated as a function of the orientation of the stripes with respect to the magnetic field. The 300-nm wide stripes are fabricated by means of electron-beam lithography and subsequent ion milling. The orientational dependence of the exchange bias shows that the shape anisotropy of the stripes can project out a component of the unidirectional anisotropy established by the field cooling. Numerical simulations with a coherent rotation model illustrate a rich phase diagram with a particularly interesting region where the shape anisotropy is slightly smaller than the unidirectional anisotropy. In this case exchange bias can even be observed with the applied field perpendicular to the cooling field direction. This approach can be used to establish different preferred magnetization directions in patterned structures with the same magnetic history.

Spin excitations of magnetic vortices in ferromagnetic nanodots: We investigated the spin-wave excitations of the magnetic vortex state in nanodot arrays in order to complement our fundamental understanding of the vortex ground state. Permalloy nanodot arrays were fabricated via e-beam lithography and lift-off procedures, and probed via Brillouin light scattering combined with numerical and analytical calculations of the dynamic magnetization. The results confirm the magnetostatic nature of the observed excitation modes that are inhomogeneous at the dot edge compared to a higher-frequency, relatively uniform mode.

Program Impact:

This program was started as a new initiative in mid-FY01 as a winner of the DOE-BES competition entitled: Complex Systems: Science of the 21st Century. It is a focal point of the nanomagnetism theme at Argonne's Center for Nanoscale Materials.

Interactions:

This program involves collaborations within MSD and throughout the world.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Since 2001 a group total of over 55 invited talks and 25 invited participation as co-organizer or program committee member of major nat'l/internat'l mtgs (*i.e.* MRS, APS, AVS, MMM, DOE, NSF.)

Personnel Commitments for FY2002 to Nearest +/- 10%:

S. Bader (20%), M. Grimsditch (20%), A. Hoffmann (100%), Dongqi Li (20%), V. Novosad (100%), J. Pearson (40%), V. Vlasko-Vlasov (10%), Hau Wang (20%), U. Welp (10%); Catherine Han (postdoc-100%).

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$ 0

FY01 BA \$ 880 K

FY02 BA \$ 955 K

FWP and possible subtask under FWP:

Superconductivity and Magnetism

FWP Number: 58906

Program Scope:

We examine the static and dynamic behavior of collective ordered states of charges and spins. Our studies of magnets and superconducting vortices are mutually reinforcing through physical analogies between the pinning and motion of domain walls and vortices, through common experimental techniques, and through similar physical effects of disorder and confinement. Our program integrates advanced theory and experiment in a single effort. Currently we focus on the new superconductor MgB_2 , confinement effects in patterned magnets, magnetic exchange coupling across interfaces, and static and dynamic phase transitions in magnetic and vortex systems.

Major Program Achievements (over duration of support):

Patterned magnets: Magneto-optical imaging (MOI) shows that a square array of submicron holes in Permalloy creates a complex network of non-collinear domains within each unit cell of the hole lattice. Magnetization reversal occurs by a novel *discrete* process of domain-by-domain flipping of the non-collinear moments. In Co rings, two magnetization states are observed. Imaging studies establish the interaction/switching behavior of these systems for possible memory applications.

Magnetic Nano-wires: Ni nano-wires with diameters of less than 100 nm were fabricated by electrodeposition into AAO templates. The magneto-transport properties of single wires reveal sharp switching of the magnetization at the coercive field. Exchange coupled magnetic bilayers: a novel MOI technique was developed for imaging the direction of the magnetization in thin films. Application to soft/hard bilayers of Fe on Sm_2Co_7 showed the breakdown of exchange locking of the soft/hard moments across the interface after application of sufficiently large reversal fields.

Vortex phase diagram: The interaction of superconducting vortex lattice, liquid, and glassy phases was revealed in systematic studies of the phase diagram of vortex matter in YBCO in the presence of controlled disorder. The evolution of a lattice to a Bose glass with disorder was characterized, and the disorder threshold needed to destroy first order melting was determined. A new phase transition line in the vortex liquid was identified in specific heat measurements. Theoretical studies of crossing lattices of pancake and Josephson vortices in BSCCO reveal a rich phase diagram of phase separations into stripe phases of lattices and chains. MOI directly revealed the strong coupling of the pancake and Josephson vortices.

Vortex dynamics: Theoretical studies of moving Josephson vortices reveal nontrivial velocity dependent structures evolving from a stretched triangular lattice to a rectangular structure at high velocity with an unstable region in between. A novel experiment in YBCO with a Corbino disk geometry enabled observation of hydrodynamic motion of the vortices.

MgB_2 : Scanning tunneling microscope studies revealed the field and temperature dependence of the two energy gaps in dense polycrystalline and thin film samples. The complete superconducting phase diagram of micron-sized MgB_2 single crystals was obtained from transport, magnetization and specific heat measurements.

Program Impact:

Our experimental and theoretical work on vortex matter and MgB_2 is recognized worldwide. In 1998 five of us won the University of Chicago Award for Distinguished Performance at Argonne, the highest scientific recognition of the Laboratory. In the past three years we have given 46 invited talks and published more than 100 papers in refereed journals.

Interactions:

We maintain strong ties with other programs in MSD (58701, Neutron and X-ray Scattering; 58916, Emerging Materials; 58823, Mesoscopic Superconductivity; 58840, Laterally Confined Nanomagnets; 58918, Magnetic Thin Films; and 59002, Materials Theory Institute) as well as with over 30 collaborators worldwide.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

American Physical Society fellowship to U. Welp.

Personnel Commitments for FY2002 to Nearest +/- 10%:

W. K. Kwok 60% G. Karapetrov 15%, A. E. Koshelev 25%, M. Iavarone 30%, Z. Xiao 35%, V. K. Vlasko-Vlasov 75%, V. M. Vinokur 20%, U. Welp 70%, D. Rosenmann 50%, H. Claus 50%, A. Rydh 100%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$ N/A

FY01 BA \$ 770K

FY02 BA \$ 796K

FWP and possible subtask under FWP:

Emerging Materials

FWP Number: 58916

Program Scope: We study the fundamental science of complex oxides exhibiting collective electronic behavior. This strategy requires the synthesis and crystal growth of exceptionally pure and uniform samples. Tunneling, transport and numerous collaborations, help elucidate the mechanisms of high- T_c superconductivity and the short- and long-range order in manganites. The influence of short-range phenomena on macroscopic physics is one highlight of this program that will use scanning tunneling to address real-space short-range behavior. Examples of future directions include exploring how spin states interact with charge and spin degrees of freedom in cobalt oxides and how anti-site defects in titanium oxides are responsible for colossal dielectric enhancement. Our tunneling and isotope effect data on MgB_2 has motivated us to search for other covalently-bonded layered materials with unfilled bands as candidates for high T_c . Electrochemical methods generate high-fugacity reactants at the electrodes and we are developing these at moderate temperatures to gain considerable flexibility and control in doping.

Major Program Achievements (over duration of support):

Our tunneling data on high T_c $Bi_2Sr_2CaCu_2O_y$ taken together with photoemission and neutron scattering data of others, provide the strongest case yet for resolving the pairing mechanism and show strong evidence for a specific non-phonon mechanism of superconductivity that is due to coupling to spin excitations. Our unique approach (with Naturally Layered Manganites, FWP 58802) to measuring transport in the highly anisotropic manganites enabled seminal results, including validation of the double-exchange, development of a simple spin-wave model including double exchange and demonstrating the metallic nature of conduction below T_c . Crystal growth of the $Pr_{0.7}Ca_{0.3}MnO_3$ system has enabled parallel scattering and bulk measurements to reveal a phase segregation that challenges theoretical models and emphasize the importance of lattice strain to phase competition in CMR materials. We have clarified the synthesis method of MgB_2 . The reported sample variability is due to impurities coupled with intergranular stresses and not nonstoichiometry. Our tunneling data first identified self-energy effects originating from interband quasiparticle scattering and our isotope effect deviates from a simple sp, phonon-mediated superconductor in a manner that is not yet explained. These results underscore the richness of MgB_2 .

Program Impact:

Our synthesis and crystal growth facilities and expertise are world renowned, as evidenced by our exemplary record regarding collaborators (50) and publication citations (>1100 in the past three years). Our efforts squarely address the most exciting scientific issues for internal programs as well as those of external collaborators. Our tunneling and anisotropic transport measurements are at the cutting edge of research worldwide because they address 'hot' scientific issues using the highest quality samples and forefront techniques developed here. In three years, our research has produced over 75 refereed papers of which 16 are high visibility journals (PRL, Nature or Science), four invited review chapters and 32 invited talks, of which eight were at major international conferences.

Interactions:

We make substantial use of major user facilities at ANL such as the Intense Pulsed Neutron Source, the Advanced Photon Source and the Electron Microscopy Center. Transport data on the layered manganites are obtained collaboratively (Naturally Layered Manganites, 58802). Tunneling studies of the high- T_c materials benefited from numerous extended visits by scientists from abroad. We have over 50 collaborations, mostly with universities, and samples sent to more than 30 institutions that have all resulted in publications.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

John F. Mitchell received one of the prestigious Presidential (and DOE) Early Career Awards in 2000. Kenneth E. Gray and John F. Mitchell were elected as Fellows of the American Physical Society in 2000 and 2002. David G. Hinks is listed among the ISI 100 most-highly-cited researchers in physics for the period 1981-1999.

Personnel Commitments for FY2002 to Nearest +/- 10%:

K.E. Gray (group leader) 75%, J.F. Mitchell 50%, H. Zheng 50%, D.G. Hinks (staff term appointee) 40%
J.F. Zasadzinski (visiting scientist from Illinois Institute of Technology, Chicago) 20% with no charge to DOE
L. Ozuyzer (visiting scientist from Izmir Institute of Technology, Turkey) 25% of which 10% paid by DOE
H. Schmidt (student) 100%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$560

FY01 BA \$499

FY02 BA \$467

FWP and possible subtask under FWP:

Magnetic Films

FWP Number: 58918

Scope: The goals of this program are to synthesize, characterize and study physical and metallurgical properties of artificially layered superlattices, double superlattices, sandwiches, wedges, ultrathin films, surfaces, high-energy-product permanent magnet films and other novel magnetic exchange coupled heterostructures. We explore modifications of materials properties as a function of preparation conditions and film thickness for films grown via sputtering and molecular beam epitaxy. We explore spring magnet heterostructures, permanent magnet films, giant magnetoresistive (GMR) materials, magneto-optic films, and magnetic heterostructures formed with superconductors, insulators and antiferromagnets. We utilize the surface magneto-optic Kerr effect (SMOKE) and synchrotron radiation as probes of magnetic films, and operate Brillouin and Raman scattering facilities as Division resources. We study basic magnetization, magnetotransport, and magneto-optic phenomena.

Major Program Achievements (over duration of support):

Non-Collinear Magnetic Structures: The surface spin flop transition provides a novel magnetic system that complements our work on spring magnets and exchange bias. Our earlier pioneering experiments stimulated renewed theoretical interest so that our new goal was to provide the layer-by-layer evolution of this inhomogeneous transition as a function of applied field. We studied an antiferromagnetic (AF) superlattice of Fe/Cr(211) via polarized neutron reflectometry. A domain wall created near the surface penetrates the superlattice with increasing field, splitting it into two anti-phase, AF domains. After reaching the center, the spin flop spreads throughout the superlattice. These new results are in substantial agreement with theoretical predictions. We then extended our investigations to artificially layered Fe/Gd ferrimagnets near the compensation temperature (where the two sublattice magnetizations cancel) via grazing-incidence x-ray magnetic circular dichroism at the APS. We confirmed the existence of a novel, non-collinear (twisted) magnetic state for Fe-terminated, but not Gd-terminated multilayers and monitored the field evolution of the (in-plane) twist.

Interfacial Tailoring of Exchange-Spring Nanocomposite Permanent Magnets: We demonstrated a new route to improve exchange-spring magnets. Epitaxial Sm-Co/Fe thin-film bilayers were annealed or deposited at high temperatures to induce interfacial mixing. The thermal processing enhances the nucleation field and the energy product. The hysteresis loop becomes more single-phase-like yet the magnetization remains fully reversible. Model simulations assuming a graded interface produce demagnetization behaviors similar to experimental observations. The graded interface also pins reversal within the soft region to potentially improve magnetic stability.

Program Impact:

Coordinate DOE CSP for Nanocomposite Magnets; provider of novel samples.

Interactions:

This program involves collaborations within MSD, IPNS, XFD-APS and throughout the world.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

2001 AVS Thornton Award (SB); since 2001 a group total of 55 invited talks and 25 invited participation as co-organizer or program committee member of major nat'l/internat'l mtgs (*i.e.* MRS, APS, AVS, MMM, DOE, NSF.)

Personnel Commitments for FY2002 to Nearest +/-10%:

S. Bader (50%), M. Grimsditch (80%), J. Samuel Jiang (90%), Dongqi Li (80%), J. Pearson (60%), J. Coble (secretary-50%).

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA: \$1,182 K **FY01 BA:** \$1,095 K **FY02 BA:** \$1,013 K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020203

FWP and possible subtask under FWP:
Advanced Materials Characterization

FWP Number: 58936

Program Scope:

The Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) includes scientists from the Chemistry and Materials Science Divisions at Argonne National Laboratory (ANL), researchers from the ANL geophysics program, and scientists from the Department of Physics at Northern Illinois University. BESSRC CAT has developed and instrumented two sectors at the Advanced Photon Source (APS) to serve the research needs of this community with particular interests in materials sciences, chemical science, atomic physics, solid-state physics, and geosciences. The facility is made up of seven separate instrumental stations, five of which operate simultaneously. The Undulator beam line (12ID), bending magnet beam line (12BM), Magnetic Compton Scattering station (11ID-B), High Energy Diffraction station (11ID-C) and High Flux Scattering Station (11ID-D) are operational. The BESSRC beam lines host numerous researchers from other national laboratories, U.S. universities and industries as well as foreign visitors through the APS General User program.

Major Program Achievements (over duration of support):

BESSRC staff have significantly improved the x-ray optics and experimental station hardware and software while operating the five BESSRC beam lines. Upgrades to the cryogenically cooled double crystal monochromator for 11ID-D have provided significant improvements in beam stability while maintaining high flux for spectroscopic and scattering experiments. The result is a monochromator which is accurate and stable and over a large energy range (4-40 KeV). Improvements to the small angle scattering instrumentation by the BESSRC staff have increased the productivity of the facility impacting the way in which small angle scattering data are taken and treated. BESSRC design efforts have been directed toward the addition of a white light mirror to 12ID for future real-time SAX detectors presently in development.

Program Impact:

Research at BESSRC CAT has been the basis for more than 170 papers. Researchers from more than one half of the groups in MSD have done experiments at BESSRC. The BESSRC beamlines have been host to 172 independent investigators and collaborators from more than 130 different institutions. More than 35 students have participated in experiments at the BESSRC facility.

Interactions:

Internal -- MSD programs: Synchrotron Radiation Studies (58926). Neutron and X-ray Scattering (58701), Superconductivity and Magnetism(58906), Basic Ceramics(58303), Interfacial Materials Chemistry, and Thin Film Magnetism. Chemical Sciences: GeoSciences and programs in the Chemistry Division. Intense Pulsed Neutron Source

External -- Oak Ridge National Lab, Brookhaven National Lab, Lawrence Berkley National Lab, Stanford Synchrotron Radiation Lab, numerous US and foreign universities and research laboratories (full listing attached).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2002 to Nearest +/- 10%:

K. Attenkofer (100%), M. A. Beno (100 %), M. Engbretson (100%), G. Jennings (100%), C. Kurtz (100%), J. Linton (100%), J. Cowan (50%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$930k

FY01 BA \$941k

FY02 BA \$954k

FWP and possible subtask under FWP:
Condensed Matter Theory

FWP Number: 59001

Program Scope:

Condensed matter theory research programs in MSD are currently carried out in the general areas of superconductivity, spectroscopy, and magnetism, with emphasis on interaction with various experimental programs within MSD.

Future plans involve theoretical support in the emerging area of nanoscience. More detail is available at <http://www.msd.anl.gov/groups/cmt/index.html>

Major Program Achievements (over duration of support):

Superconductivity. Calculated dynamic susceptibility to explain inelastic neutron scattering results on the cuprate superconductor YBCO. Formulated theory of c-axis transport in cuprates based on resonant tunneling to explain data in the pseudogap phase. Constructed model of ferromagnetic superconductivity to address experiments in UGe₂. Explained optical sum rule violation in the cuprates as due to the appearance of quasiparticle states in the superconducting phase, implying kinetic energy lowering.

Spectroscopy. Calculated ARPES spectra in the superconducting phase of cuprates assuming interaction of the electrons with the magnetic resonance. Used ARPES results showing bilayer splitting to infer symmetry of the resonance. Refuted recent claim that the resonance does not have enough weight to affect spectral properties. Discovered presence of a new crossover line in cuprates separating Fermi liquid phase from strange metal phase based on loss of coherence in ARPES and resistivity data.

Magnetism. Formulated quantum interference corrections to the conductivity of quasi-2D metals. Explored metal insulator transition in cuprates as a consequence of formation of a spin density wave state. Explained jump in the Hall number at the quantum critical point of vanadium doped chromium as due to loss of flat Fermi surfaces from nesting driven magnetism.

Program Impact:

Work, particularly in the area of superconductivity, is recognized world-wide, with numerous invited talks given by Drs. Abrikosov and Norman. The collaboration on photoemission in cuprate superconductors in the past several years led to 3 papers in Nature, 14 in PRL, and 16 in PRB. Paper in Nature on the pseudogap in 1996 has over 600 citations, and at one time was listed as the top cited paper in physics.

Interactions:

This program involves collaborations with ANL Materials Science programs on Superconductivity and Magnetism (58906), Magnetic Thin Films (58918), Photon Science at Synchrotrons (58926), Neutron and X-Ray Scattering (58701), Naturally Layered Manganites (58802), Laterally Confined Nanomagnets (58830), and Emerging Materials (58916); and with university programs at the University of Chicago, University of Illinois at Chicago, Northern Illinois, Notre Dame, and SPhT-Saclay.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Dr. Abrikosov was elected to the National Academy of Sciences and the Royal Society of London. Dr. Norman received the University of Chicago Distinguished Performance Award.

Personnel Commitments for FY2002 to Nearest +/- 10%:

A. Abrikosov (100%), M. Norman (100%), R. Ramazashvili (100%); V. Vinokur (50%); A. Koshelev (50%); M. van Veenendaal (20%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$872

FY01 BA \$847

FY02 BA \$904

FWP and possible subtask under FWP:

Condensed matter theory, theory of advanced materials

FWP Number: 59002

Program Scope:

Materials Theory Institute brings leading theorists to Argonne from the USA and international community for stays from two weeks to one year to focus on the most exciting current topics in condensed matter research. The topics are selected by the Institute to coincide with Argonne's key scientific directions, drawing powerful theoretical support from the best scientists in the field to the Laboratory's doorstep. The main directions covered are:

Physics of vortex matter at extreme scales and conditions.

Soft condensed matter, granular materials, and fractures.

Nanoscale superconductivity and magnetism.

Major Program Achievements (over duration of support):

A theory of the dislocation-mediated melting and non-linear dynamics in strongly disordered materials is put forward. A theory of surface-disorder induced pinning is developed. A theory of a complex vortex state, crossing lattices is developed.

A theory of transport in point superconducting contacts is developed.

A theory of ballistic transport in nanoscale-size superconductors is developed. The predicted effects of alternating conductance controlled by an external magnetic field offers an opportunity for low-dissipative quantum switch in quantum transport.

A theory of dc and ac critical depinning in magnets is developed.

A continuum description of charged granular matter is developed.

Advances in understanding magnetic nanostructures: description of tunable superheating and supercooling in magnetic multilayers, investigations of normal modes of nano-sized particles magnetization of an array of square holes in a rotating field.

A spintronic device configuration whose magnetization direction can be controlled by an external applied voltage has been proposed.

A theory for reversible magnetic switching of point magnetic heterostructures by an external bias is developed.

Program Impact:

Our work on nanoscale superconductivity and magnetism is recognized worldwide. Theories of avalanches in granular materials and the theory of charged granular dynamics are viewed as major recent advances in the field. About 40 leading scientists in the field of nano-scale superconductivity and magnetism, granular physics, and nonlinear physics were hosted during the past three years, resulting in about 50 publications and 20 invited talks. An International Workshop on Nanoscale Superconductivity and Magnetism was held at Argonne in 2001, and an International Workshop on Nanoscale Superconductivity and Magnetism is hosting about forty world-leading specialists in October-November 2002.

Interactions:

Harvard Univ., Syracuse Univ., LANL, Köln Univ., Leiden Univ., Univ. of Florida, UCSD, Texas A&M Univ., Helsinki Univ., Bar-Ilan Univ., Israel, Weizmann Res. Inst., Israel, Ecole Polytechnique, France, and Univ. of Wisconsin. Long-term joint research programs established with Lorentz Center at Leiden Univ., Oslo Univ., Delft Univ., ETH, Zurich, and AF Ioffe Inst., St. Petersburg, Russia.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

American Physical Society fellowship to I. Aronson.

Personnel Commitments for FY2002 to Nearest +/- 10%:

V. Vinokur 20%, I. Aronson 10%, A. Koshchev 10%, D. Feldman 50%, A. Lopatin 100%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$ N/A

FY01 BA \$ 150K

FY02 BA \$ 276K

FWP and possible subtask under FWP:

Nanostructured Thin Films

FWP Number: 57504

Program Scope: Ultrananocrystalline diamond (UNCD) thin films encompass experimental and theoretical studies of diamond thin film growth processes, film morphology, grain boundary geometric and electronic structure, and their relation to structural, mechanical, electronic, electrochemical, tribological, and thermal transport properties. Complex oxide thin films and heterostructures includes studies of perovskite oxide and oxygen barrier film-growth and interface processes; hydrogen/oxygen annealing effects and diffusion barrier materials. The growth of high dielectric constant oxides and interface formation in oxide thin films on silicon substrates is also of particular interest. Quantum chemical methods play a crucial role in this program, and frequently theory and experiment are coordinated on common scientific problems in a material system. Various state-of-the-art electronic structure methods are being used, including *ab initio* molecular orbital theory and density functional based tight binding molecular dynamics. Computational studies have provided valuable insight into the effect of nitrogen on the UNCD growth mechanisms

Major Program Achievements (over duration of support):

Ultrananocrystalline Diamond: Tuning Materials Properties via Plasma Chemistry. Ultrananocrystalline diamond (UNCD) is grown using microwave plasma chemical vapor deposition (MPCVD) and consists of ultra-small (2-5 nm) grains and atomically abrupt grain boundaries. UNCD films are phase-pure, and can be conformally coated on high aspect ratio structures on a variety of materials. UNCD has been found to have many unique materials properties, several of which are tunable via the precise control of plasma chemistry.

Complex Oxide Heterostructures. In situ mass spectroscopy of recoil surface analysis and X-ray photoelectron spectroscopy were used to study oxidation processes in amorphous and crystalline TiAl and TiAlN layers. XPS revealed the formation of TiO₂ on the surface of TiAlN at 500-600°C and on TiAl at 600-700 °C. making the latter more resistant to oxidation. Electrical characterization of PZT capacitors demonstrated that the TiAl provides a good diffusion barrier layer for integration of PZT capacitors with Si substrates.

Modeling of UNCD grain boundary electronic structure. Density-functional based tight-binding molecular dynamics calculations of high-energy high-angle twist (100) diamond grain boundaries with and without nitrogen impurities have been performed. We found that about one-half of the carbons in the grain boundary are threefold coordinated and are responsible for states introduced into the band gap. This work suggests that GB conduction via carbon π -states in the GB is responsible for the high electrical conductivities in nitrogen-doped UNCD films.

Program Impact:

UNCD is finding many potential applications as cold-cathode electron sources, tribomechanical coatings, biochemical electrodes, and microelectromechanical systems (MEMS).

Interactions:

In addition to extensive collaborative relationships within the Materials Science Division, major facilities used are the Advanced Photon Source, and the Electron Microscopy Center (ANL), the Advanced Light Source (Berkeley, CA), the Materials Research Laboratory (UIUC), and the Synchrotron Radiation Center (Stoughton, WI).

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Over the past three years over 40 publications, over 15 invited talks, and two plenary talks have resulted from this work. The 2000 MRS Award was presented for the development of UNCD at ANL over the past ten years.

Personnel Commitments for FY2002 to Nearest +/- 10%:

J.A. Carlisle (??%), L.A. Curtiss (??%), D.M. Gruen (??%), M. Angadi (??%)

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$887

FY01 BA \$875

FY02 BA \$902

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:

FWP Molecular Materials

FWP Number: 57525

Program Scope:

This project involves the design, synthesis, and characterization of nanostructured materials incorporating biomolecule arrays that exploit the capabilities of biological molecules to store and transduce energy.

Use polymer-grafted, lipid-based complex fluids for the formation of functionally-active, hierarchically-structured and vectorial-ordered arrays of proteins in synthetically-derived scaffolds.

The integration of the proteo-complex fluids into rigid mesoporous inorganic frameworks and modification of the frameworks to tailor electronic transport and photon-induced processes between the biomolecules and the host.

The interfacing of the proteo-complex fluids with carbon based electrode surfaces and modification of the interface to tailor field-induced ionic transport processes at the interface.

Major Program Achievements (over duration of support):

This program was initiated in the last quarter of FY02.

Program Impact:

The program encompasses a novel approach to the development of nanostructured biomaterials that exploits biological functions. We expect the results of our research to provide fundamental insight into how to use soft and hard materials to construct complex architectures that combine the functionality of biomolecules with the novel properties of the host materials. The project will also provide fundamental knowledge of the nanoscale phenomena occurring at the interfaces of these integrated materials and how to tailor energy transduction processes. The fundamental information gained will lay the ground work for the next generation materials for use in sensors, optoelectronics, artificial organ replacement, or catalysis.

Interactions:

Internal—Center for Nanoscale Materials, Biosciences Division, Chemical Technology Division, Advanced Photon Source, Intense Pulse Neutron Source,

External—Northwestern University, University of Wisconsin, Northwestern University

Recognitions, Honors and Awards (at least in some part attributable to support under this program):

This program was initiated in the last quarter of FY02.

Personnel Commitments for FY2002 to Nearest +/- 10%:

This program was initiated in the last quarter of FY02 with funds being used for lab setup. M. Firestone (coordinator), D. Gruen, L. A. Curtiss, R. Gerald, P. Labile

Authorized Budget (BA) for FY00, FY01, FY2002:

FY00 BA \$ 0 k

FY01 BA \$ 0

FY02 BA \$300 k

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:

FWP Molecular Materials

FWP Number: 58510 (includes 57502)

Program Scope:

Basic research aimed at synthesis of materials whose unique properties originate at the molecular level. The types of materials include (1) patterned surfaces and thin films from soft matter such as diblock copolymers and organic metals for molecular and/or hybrid electronics. (2) nanoparticle composites to exploit the novel properties of organized arrays of nanoparticles for electronic, magnetic, or photonic applications. (3) nanoporous materials for use as catalysts, hosts for clusters, and templates for nanowires, nanotubes, nanodots, etc. In addition, advanced experimental and theoretical techniques at Argonne user facilities are used for characterization.

Major Program Achievements (over duration of support):

A new electrodeposition method was discovered that is capable of making conductive thin films of organic charge-transfer salts for the first time. The structure and molecular packing of the OPV-PEG system diblock co-polymer system has been determined, that will allow manipulation of nanofibers to create nanomagnetic arrays.

Demonstrated facile introduction and spatial compartmentalization of inorganic nanoparticles in a complex fluid medium. Demonstrated that post-self-assembly processing employing magnetic fields can be effectively used as a means to extend order in self-assembled systems. An in situ X-ray study at the APS has shown unexpected ordering in colloidal gold nanoparticles systems present prior to formation of order arrays on surfaces.

The structure of selenium encapsulated in zeolite hosts point to the presence of strongly disordered, isolated Se_x chains resulting in the creation of charge-transfer states. Crystal engineering has been employed to design specific patterns of intermediate-range order within amorphous zinc-chloride networks. Accurate synthetic control of the pore structure of anodized aluminum oxide is being used to make nanowires.

The G3 theoretical methods were developed and represent a new level of accuracy for calculation of energies, which is being widely used in the scientific community and in work in this project .

Program Impact:

The synthesis effort is leading to new and exciting nanostructured materials with potential for electronics, optics, and photonics applications. Our unique capabilities in design and fabrication of new materials has led to close interaction with other groups in the Materials Science Division as well as the worldwide scientific community. Our work on organic conductors and on theoretical methods is recognized world-wide.

Interactions:

Internal— Materials Science Division (Superconductivity Group, Magnetism Group, Surface Chemistry Group), Biomolecular Materials NSET initiative, Center for Nanoscale Materials, Chemistry Division, Advanced Photon Source, Intense Pulse Neutron Source, Math and Computer Science Division

External— Over 30 universities including the University of Chicago, Washington University, Michigan State University, Paderborn University, Northwestern University.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Organized 4 international symposia, over 100 publications (including 2 Nature and 6 Physical Review Letter papers), 4 invited review chapters, over 30 invited talks. Organic superconductor research was named one of the 100 top scientific discoveries funded by the DOE Office of Science. Numerous citations to papers including one group member named a Highly Cited Researcher in Chemistry by ISI.

Personnel Commitments for FY2002 to Nearest +/- 10%:

H. Wang (80%), J. Schlueter (100%), U. Geiser (100%), M. Firestone (50%), X-M. Lin (10%), L. E. Iton (100%)
L. Curtiss (10%), Saboungi (10%)

Authorized Budget (BA) for FY00, FY01, FY2002:

FY00 BA \$1377 K

FY01 BA \$1267 K

FY02 BA \$1163 K

Laboratory Name: Argonne National Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Directed Energy Interactions with Surfaces

FWP Number: 58600

Program Scope: Using world-class tools, this program seeks to develop a predictive understanding of the effects of directed energy sources (ions, electrons, and photons) on the composition, structure, and material properties of surfaces and other materials whose dimensions are of atomic scale. These tools, based on laser postionization of atoms and molecules desorbed by directed energy sources have been developed at ANL and provide the program with uniquely sensitive methods for trace analysis of surfaces, nano-materials, and for probing particle-surface and laser-surface interactions.

Major Program Achievements (over duration of support):

Fundamentals of Particle Desorption: The interaction of lasers with transparent solids is of crucial importance in the area of optical damage. Using uniquely engineered surfaces we have examined the interaction of light with quartz substrates containing of gold nanospheres immersed at various depths into the substrate. Our results clearly demonstrate that surface atom ejection arises from a complex sequence of cumulative damage, rather than from single shot damage as has previously been suggested.

Trace Analysis of Samples with Atomic Dimensions: The unique combination of high useful yield (atoms detected/atoms removed) and high discrimination provided by the Resonant Ionization Mass Spectrometers developed under this FWP, allow for the first time trace analysis of samples containing only a few atoms of the analyte of interest. A new instrument has just been put into operation which combines useful yields in excess of 0.3 (compared to state of the art large frame SIMS instruments with useful yields $\sim 10^{-3}$ – 10^{-5}) with the ability to measure at concentrations down to 1 part per trillion (ppt).

Molecular Surface Analysis: Building on earlier work demonstrating that one-photon vacuum ultraviolet (VUV) photoionization can provide a fragmentation free method for analysis of large molecules, the highest reported molecular useful yield (0.005) was obtained using an F₂ excimer laser with sufficient intensity to saturate the photoionization volume. Currently efforts are underway to combine the high pulse energy, tunable VUV from the 4th generation light source at ANL with a microfocus ion probe mass spectrometer to provide a small spot (100 nm), sensitive, and discriminative probe of the molecular content of a surface or nanometer-scale object.

Program Impact:

This work has resulted in numerous invited talks and publications including articles in Science and Physical Review Letters. Work here continues to be a world leader in understanding the interaction of energetic ions, photons and electrons with surfaces. The microfocus ion probe mass spectrometer developed under this FWP is the most sensitive in the world, particularly when applied to samples containing limited numbers of atoms or molecules.

Interactions:

Collaborative publications with a wide range of University (including University of Chicago, Washington University St. Louis, California Institute of Technology, University of Newcastle) and National Labs (ANL, SNL, and LLNL) have appeared in the last few years. Further, our unique tools are applied in collaborative research on problems of particular importance to DOE. This work includes studies of optical damage with the National Ignition Facility and studies of surface oxidation and corrosion with both SCLTR and the Office of Industrial Technologies' Aluminum Vision.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Fundamental laser desorption work in this area received the Energy100 Award for the discovering that 308 nm Excimer Laser removes organic material by electronic excitation - one of the Department of Energy's top scientific contributions of the 20th century.

Personnel Commitments for FY2002 to Nearest +/- 10%:

M. J. Pellin 100%, W. F. Calaway 100%, D. M. Gruen 50%

Authorized Budget (BA) for FY00, FY01, FY02:

FY00 BA \$736

FY01 BA \$625

FY02 BA \$610